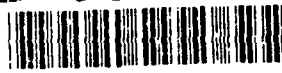


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The Interaction of HCN/DCN with Si(100)-2x1

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## Abstract

We have investigated the spectroscopy and reaction of HCN (DCN) adsorbed on Si(100)-2x1 at  $T_s \geq 100$  K using high resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS). HCN (DCN) formed dimers and/or polymers on the surface at 100 K and higher dosages ( $D > 4$  L). The HREEL spectrum obtained after warming a 4.5 L HCN dosed surface to 200 K resembles that obtained with a lower HCN dosage ( $D < 0.6$  L). Two major species, HCNH and CN, could be identified from this spectrum. The former species showed peaks at 160, 368, and  $\sim 400$  meV for HC=NH, CH, and NH stretching vibrations, respectively, while the latter showed a peak at 263 meV due to the C $\equiv$ N stretching vibration. In the corresponding DCN experiment, the DC=ND stretching mode was observed at 124 meV. Annealing the sample at 560 K appeared to cause the reorientation of the CN radical from an "end-on" to a "side-on" adsorption geometry as evidenced by HREELS, UPS, and XPS analyses. At 600-800 K, the breaking of CH, NH and CN bond occurred on the surface. Above 1000 K, only C and N species remained on the surface following the complete dissociation of CH, NH, and CN bonds and the desorption of H species.

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## Introduction

Hydrogen cyanide (HCN) and some other related molecules, e.g.,  $C_2N_2$ ,  $(CH_2NH_2)_2$ , have been studied on several metals, primarily with high resolution electron energy loss spectroscopy (HREELS), ultraviolet photo-electron spectroscopy (UPS) and temperature-programmed desorption (TPD) techniques.<sup>1-14</sup> On Pd(111) at  $T_s < 140$  K, HCN forms dimers at  $\sim 1$  L dosage and multilayers at higher dosages. Above 300 K, no  $C\equiv N$ -species was observed, instead an  $H-C=N$ -species with the HCN bond angle less than  $180^\circ$  and the CN bond parallel to the surface plane was detected to be the dominant adsorbed species.<sup>1</sup>  $C_2N_2$  also adsorbed on Pd(111) at 120 K with its molecular axis parallel to the surface plane; above 300 K, the C-C bond broke to give two adsorbed CN species with side-on geometry.<sup>2</sup> For HCN on Pt(111), two adsorption states could be identified at 200 K according to the  $N_{1s}$  XPS study; one of them is believed to interact with the surface through nitrogen lone electron pairs.<sup>3</sup> Such an adsorbed state was also assumed by Hagans et al.<sup>4</sup> because of the observed large negative surface work function change upon HCN adsorption on Pt(111). Furthermore,  $C_2N_2$  was found to react with  $H_2$  on Pt(111) at 250 K and diimine was identified as the intermediate.<sup>3,5</sup> Similar studies were also carried out for HCN on Cu(111).<sup>6</sup> Interestingly, preadsorption of  $O_2$  on this surface had a noticeable effect on CN adsorption and caused the reorientation of the CN species from a side-on to end-on geometry.<sup>7</sup>

Although HCN and its related species have been fairly well studied on some metal surfaces, very little has been reported on the interaction of these molecules with semiconductors. Since small molecules, such as  $NH_3$ <sup>15</sup>,  $O_2$ <sup>16</sup> and  $Cl$ <sup>17</sup>, etc., were found to interact differently with different Si substrates, the behavior of HCN on Si surfaces may also be affected by surface structure. Thus a study of HCN on different Si single crystals may provide more information about the Si structural effect on

reactivity as well as the HCN surface chemistry on Si in general. In addition, the formation of  $(\text{CN})_x$  film, if it is possible at all, would be of interest to microelectronic device applications.

In this work we report the results of HCN (DCN) interaction with Si(100)-2x1 in the temperature range 100 -1000 K, as studied by HREELS, UPS and X-ray photoelectron spectroscopy (XPS).

## Experimental

The experiment was carried out in a custom-designed UHV system with multiple surface analysis capabilities as described elsewhere.<sup>18,19</sup> A 2" diameter B-doped Si(100) single crystal wafer from Virginia Semiconductor Inc. was cut into 1.5x1.0 cm<sup>2</sup> samples. The samples were chemically cleaned with hot 5% HF solution and rinsed with deionized water. After being introduced into the UHV chamber, the Si surface was annealed repeatedly to  $T_s > 1500$  K until no impurities, such as C, N and O, etc., could be detected by AES, XPS and HREELS. In the HREELS experiment, an electron beam with a primary energy of 5 eV and a resolution of 8 meV in the straight-through mode was used. However, after scattering from the surface, the resolution was reduced to 9-12 meV (FWHM) as measured from the elastic peak. Typical rate counts for the elastic peak from clean Si(100) at 100 K were  $3\text{-}4 \times 10^5$  counts/sec.

HCN and DCN were prepared by acidifying *in vacuo* dry sodium cyanide with 60%  $\text{H}_3\text{PO}_4$  and  $\text{D}_3\text{PO}_4$  ( $\text{D}_2\text{O}$ ) solutions, respectively. The generated gaseous products were purified by trap-to-trap distillation through a series of traps maintained at 195, 160, and 77 K. The fraction collected at 160 K (ethanol slush) was distilled once more from 195 K (dry ice) to 77 K (liquid  $\text{N}_2$ ). FTIR (Fourier transform infrared) analyses of the prepared samples indicated no detectable impurities. The DCN sample was found to have greater than 95%-D enrichment.

## Results and Discussion

### 1. HREELS

Figure 1 shows the HREELS of HCN on Si(100)-2x1 at 100 K with different dosages. When 0.6 L HCN was dosed onto the surface, HREELS presented peaks at 80, 100, 130 (shoulder), 160, 180, 200 (shoulder), 260, 368 and 400 meV. The spectrum is rather complicated and similar to that obtained after warming the 4.5 L HCN dosed sample to 220 K. In addition to HCN, HCNH and CN radicals could be identified in these spectra as will be discussed in detail later. The molecularly adsorbed HCN, may be identified by the peaks at 80, 260 and 400 meV. These three peaks could be assigned to the HCN bending,  $C\equiv N$  and C-H stretching vibrations, respectively, by analogy to the corresponding HCN IR results<sup>20</sup> summarized in Table 1. In addition, peaks at 100 meV and its overtone at 200 meV, suggest the formation of HCN dimers on the surface, since the bending frequency at 91-98 meV was observed in the matrix-isolated HCN dimers.<sup>21</sup> In solid HCN,<sup>22,23</sup> this frequency appeared at 102 meV.

The dimeric and possibly polymeric HCN became dominant species on the surface, as more and more HCN was introduced into the system. The relative intensity of the 80 meV peak gradually decreased, while that of the 100 meV peak increased; the latter peak also shifted to 105 meV at 4.5 L dosage. At this dosage, a shoulder at 56 meV due to the overtone of the intermolecular torsional vibration expected at 20-30 meV as was observed in solid HCN<sup>21,23</sup> could be identified. Indeed, with the improved resolution (FWHM=6meV in the straight through mode) at the expense of the signal intensity, a peak at 28 meV could be resolved from the elastic peak as also shown in Figure 1 (top left). This value agrees reasonably with that of 26 meV peak reported for HCN on Cu(111) at 100 K.<sup>6</sup>

At higher HCN dosages, the intensity of the 180 meV peak decreased, while that of the 130 meV peak increased; both peaks shifted slightly towards the higher energy side with increasing HCN dosages. These two peaks could be attributed to the combinations of the 100 meV mode with 80 and 28 meV modes, respectively. Finally, the peaks at 160 and 368 meV, which will be discussed next, became weaker and the 368 meV was gradually obscured by the 400 meV peak as the HCN dosage was increased. These attenuations are likely due to the suppression effect of the HCN overlayer. The 160 meV peak may also have some contribution from the overtone of the 80 meV mode, and thus its intensity reduction is partially caused by the attenuation of the 80 meV peak. It should be pointed out that the 200 meV peak cannot be completely attributed to the overtone of the 100 meV mode either, because the former was still noticeable in the higher temperature spectra.

Figures 2 and 3 summarize the thermal effect on the HREELS of the 4.5 L HCN and DCN dosed Si(100) surfaces, respectively. At 100 K, peaks at 80, 105 (83), 130, 163, 200, 263 (238), 400 (320) and 420 (348) (shoulder) meV appeared in the HREELS of HCN (DCN). These peaks were discussed above and assigned to the HCN and/or (HCN)<sub>n</sub> ( $n \geq 2$ ) species as listed in Table III. Although the DCN sample used had >95% D-enrichment, it is very difficult to avoid the HCN species completely in the DCN experiment due to the efficient H-D exchange occurred in the system.

When the 4.5 L HCN (DCN) dosed sample was warmed to 220 K, the following changes were noted: 1. All peak intensity was attenuated by a few times and the HCN spectrum closely resembled that of the 0.6 L HCN dosed sample at 100 K. These changes indicate a partial desorption of the adsorbates, which was more directly reflected in the corresponding XPS results (see discussion in the XPS section). 2. The 100 and 130 meV peaks vanished, while that of the 80 meV became very intense in the HCN spectrum. These changes are obviously due to the breaking of the dimeric and/or polymeric HCN on the surface; 3. Interestingly, the 238 meV peak in the DCN

spectrum disappeared and the relative intensity of the 263 meV peak increased in both DCN and HCN spectra. Clearly, the C-H (C-D) bond cracking occurred at this temperature and the 263 meV peak observed here is due to the CN, but not the HC≡N species. The appearance of the CN radical suggests that Si-H may also be present. The Si-H stretching vibrational peak is known to be ~260 meV and thus could not be resolved from that of the CN stretching mode in the HCN experiment. However, this should be seen in the corresponding DCN experiment as the Si-D stretching vibrational mode should be shifted to ~200 meV. Indeed, the 200 meV peak was slightly stronger in the DCN system than HCN according to the HREELS taken at the same temperature. The comparatively weak 200 meV peak in DCN HREELS also ruled out the possibility that the 260 meV derived mainly from the Si-H species in the HCN HREELS. On the other hand, the weak Si-H mode and the increasing intensity of the 367 meV peak suggests the second species, HCNH, may appear on the surface. According to a quantum chemical calculation by Melius,<sup>24</sup> the HCNH radical has frequencies at 115 ( $\delta_{\text{HCNH}}$ ), 123 ( $\delta_{\text{CH}}$ ), 148 ( $\delta_{\text{NH}}$ ), 190 ( $\nu_{\text{CN}}$ ), 364 ( $\nu_{\text{CH}}$ ) and 407 ( $\nu_{\text{NH}}$ ) meV, respectively. The C-H stretching vibration mode matched well with the 368 meV peak observed here, while the tail at the high energy loss side of the 400 meV peak, which was shifted to ~420 meV at higher annealing temperatures, could be attributed to the  $\nu_{\text{NH}}$  stretching mode as will be further discussed later. The C=N stretching mode could probably be related to the 160 meV peak observed here, because it was shifted to 124 meV in the corresponding DCN HREEL spectra. This 36 meV isotopic shift could be accounted for by a doubly deuterated species, i.e., DCND. For a single deuterated species the shift in the CN stretching frequency is expected to be smaller, e.g., the isotopic shifts for the CN stretching mode have been reported to be from 191 to 177 [10] and 251 to 241 meV [25] in HCN (DCN) and HNC (DNC), respectively. As to the three deformation vibrations of the HCNH species, they are probably weak and obscured by the adjacent stronger peaks at 80 and 160 meV. The 160 meV peak

cannot be attributed completely to the overtone of the HCN bending mode at 80 meV for two reasons. Firstly, in the corresponding DCN experiment to be discussed later, the 160 meV peak was essentially absent; instead, a peak at 124 meV was observed at  $T_s > 220$  K, while the behavior of the 80 meV peak was similar for both HCN and DCN on Si(100). The 124 meV peak was expected to appear in the DCN system because of the isotopic shift, if the 160 meV peak was due to the  $\nu_{CN}$  stretching mode of the HC=NH radical. Secondly, the relative intensity of the 160 meV peak was weaker in lower dosage (0.4 L) spectra, most likely reflecting the lower dimer and, accordingly, HCNH concentration. Finally, the 200 meV peak is probably due to a small amount of HC=N and/or C=N species, which also existed at 100 K, since the 100 meV peak essentially vanished at this temperature.

When the sample was annealed at 560-610 K, the 263 meV peak was attenuated and shifted to 270 meV, while the 367 and 400 meV peaks shifted gradually to 375 and 425 meV, respectively. The attenuation of the 263 meV peak, without diminishing that of the CH stretching vibration, may be due to the CN desorption or, more likely, to the reorientation of the CN species from the end-on to a side-on adsorption geometry and concomitantly converting it into a C=N double bond species. The latter explanation is consistent with the corresponding UPS and XPS results as will be discussed later. The breaking of the CN bond could also cause the decrease in the 260 meV peak intensity; however, it is very unlikely to be a major process because of the strength of the CN triple bond. The remaining peak, now shifted to 270 meV, may be attributed to the combination of both Si-H and the C $\equiv$ N species survived on the surface. The shifting of the 367 and 400 meV peaks to 375 and 420 meV is ascribed to the further formation of the HC=NH species. Considering the possibility of peak shifting upon adsorption, these two modes agree reasonably with the values of 364 and 407 meV calculated for the gaseous HCNH radical. The 420 meV peak, which shifted further to 425 meV at 610 K, is somewhat higher than the



known C-H stretching or N-H stretching in HC=NH vibration frequencies. Therefore, we speculate that at these temperatures, part of HC=NH species may dissociate into HC≡N and/or HN≡C, giving rise to multiple peaks between 350 and 450 meV in the 610 K spectrum. The gaseous HN≡C molecule has a peak at 452 meV for the NH stretching vibration in the IR region (see Table II). In fact, the tails at the higher energy side of the 420 and 425 meV peaks at 560 and 610 K, respectively, extended as far as 450 meV, indicating a possible contribution from the HNC species to the 420-425 meV peak. In addition, the slight growth of the 200 meV peak at 610 K could be attributed to that of the HC=N<sup>(a)</sup> and/or the HN=C<sup>(a)</sup> adspecies. Since the peak was rather weak, these species presumably formed di-σ bonds to the surface with the C=N bonds parallel to the surface plane and C-H or N-H bond tilted about 30° from the surface normal, so as to give a relatively strong C-H or N-H stretching vibration peak, as can be seen in the corresponding HREEL spectra. The multiple peaks appeared between 350-450 meV in the 610 K spectrum, as alluded to above, indicate the concurrent presence of various CH and NH containing species on the surface. It is worth mentioning that in the HREELS of the 0.4 L HCN dosed Si(100) to be presented below, the 400 meV peak was only shifted by 10 meV to 410 meV in the same temperature range on account of a lower concentration of dimers, resulting in a smaller extent of NH formation under the lower dosage condition.

At 560 K, the 260 meV peak was also attenuated in the corresponding DCN experiment. However, other changes were less illustrative, because the DC and DN stretching modes were poorly resolved in the present study. Annealing the sample at 680 K caused a substantial cracking of the D-C and D-N bonds as indicated by the increase of the 195 meV peak, which now shifted to 200 meV mainly due to the Si-D stretching vibration and the decrease of the 313 meV peak from the C-D and N-D stretching vibrations. In addition, the reappearance of the shoulder at ~240 meV in the DCN spectrum indicates the reforming of the DC≡N species by either the combination

of D and CN species or the breaking of the D-N bond in DCND species. In the HCN experiment, the 260 meV peak was not well resolved from the 270 meV peak. Nevertheless, there is a noticeable tail at the lower energy side of the 270 meV peak in the 610 K spectrum.

As the sample was further annealed at 820 K, peaks at 100, with a shoulder at 125 meV, 272 and 375 meV were observed. These peaks are attributable to  $\text{SiCH}_x$  ( $x = 0, 1$ ), Si-N, Si-H and CH stretching vibrations, respectively, indicating the breaking of the CN bond, the NH bond and, to some extent, the CH bond. The peak at 272 meV may still have some contribution from the residual CN stretching vibration. However, it would be minor, because the 200 meV peak due to the Si-D species was fairly strong at  $T_s > 690$  K in the corresponding DCN spectra. Above 1000 K, HREELS was dominated by the 100 meV peak with a shoulder at 125 meV due to the Si-C and SiN species.

The thermal effects observed on the 0.4 L HCN dosed Si(100) (see Fig. 4) are essentially the same as those on the 4.5 L HCN dosed surface, except that the relative intensities of the 160, 200 and 368 meV peaks were weaker and that the 400 meV peak shifted only slightly towards the high energy side for the 0.4 L HCN dosed sample at temperatures between 220-610 K. These differences could be attributed to the smaller concentration of the HCN dimers and HCNH radicals on the 0.4 L HCN than the 4.5 L HCN dosed surface. At 680 K, the 265 meV peak was enhanced, likely due to the Si-H formation, because of less dimer or HCNH formation and more HCN species on the surface at low temperatures and, accordingly, more surface sites available for the HC and NH bond breaking. These observations are fully consistent with the higher dosage experimental results.

To substantiate the existence of certain species, the HREELS of 0.4 L HCN dosed Si(100)-2x1 at 100 K were recorded in both the specular (a) and 12° off-specular (b) modes as presented in Fig. 5. The 100 K spectrum is similar to that taken

from the 4.5 L HCN L dosed sample after warming up to 220 K. As discussed earlier, at least two species could be identified in this spectra, CN and HCNH species, with their CN bond perpendicular and parallel to the surface plane, respectively. These arguments could be further established from the  $12^\circ$  off-specular spectrum. The vibrational modes associated with the  $\text{-C=N-}$  bonds of the HCNH radical, i.e., peaks at 160, 368 and 400 meV, are mainly due to the impact scattering, while the 260 meV peak associated with the  $\text{C}\equiv\text{N}$  species is due mainly to dipole scattering.

## 2. UPS

Figure 6 shows the thermal effect on the UPS (He II) results for a 1.5 L HCN dosed Si(100)-2x1 surface. All the curves plotted are the differential spectra, i.e., they are obtained by subtracting the spectra taken from the dosed and annealed samples from that taken from the clean surface. When 1.5 L HCN was dosed on the surface at 100 K, peaks at 5.1, 7.7 and 12.4 eV below  $E_F$  were evidenced. In addition, a negative peak at 0.8 eV indicated the attenuation of the surface states upon the adsorption of HCN.<sup>26,27</sup> When multilayer HCN was dosed on Pd(111),<sup>9</sup> peaks at 7.4 and 13.3 eV below  $E_F$  were clearly shown in the He (I) UP spectrum. The energy separation between the two peaks correlates very well with that of the gaseous HCN UPS results, thus these two peaks were assigned to the  $1\pi$ ,  $5\sigma$  and  $4\sigma$  molecular orbitals, respectively. Here, the UPS (He II) of the 1.5 L HCN dosed Si(100) is apparently more complicated because the presence of the various adsorbed species as is clearly evidenced in the corresponding HREELS results (Figure 1). The strong peak at 7.7 eV could be attributed to the mixture of  $1\pi$  and  $5\sigma$  orbitals, while the peak at 12.4 eV with a tail extended over 13.3 eV could be assigned to the  $4\sigma$  orbital (predominantly the C-H bond character). On the other hand, the two broader peaks and their widely spread large tails are probably due to the presence of the different adsorbed species. To assign the 5.1 eV peak is somewhat difficult. It could probably

be related to the small amount of  $\text{HC}=\text{N}^{-(a)}$  and/or  $\text{C}=\text{N}^{-(a)}$  species, presumably due to the N lone electron pair. This peak was still evident at 220 K, at which such species were also present in the HREELS. Further annealing the sample to higher temperatures caused the vanishing or at least the attenuation of the peak and thus it was obscured by the more intense adjacent peak at 6 eV.

When the surface was warmed to 220 K, all peaks shifted towards the lower B.E. side with different degrees of shifting; the 7.7 eV peak intensity also decreased considerably. These changes are caused mainly by the partial desorption of the adsorbates and, as a result, the interaction between the adsorbates became weaker (especially the disappearance of hydrogen bonding, so the HCN relaxed to a lesser extent as compared with that under higher dosage conditions. Such a B.E. shift was also observed for  $\text{N}_2\text{H}_4$  on Fe(III) before and after solid  $\text{N}_2\text{H}_4$  was formed on the surface.<sup>28</sup>

Annealing the sample at 580 K caused the disappearance of the 5 eV peak, the further shifting of the 6.3 and 11.7 eV peaks towards lower binding energies accompanied by a noticeable increase of the former. A peak at 6.1 eV was also reported for a side-on CN adspecies on Pd(III)<sup>9</sup> due to the combination of the  $5\sigma$  and  $1\pi$  orbitals. Here the 6.3 eV peak could be related to such an adsorbed CN radical also. As discussed earlier in the HREELS study, at 560 K the 260 meV peak attenuated substantially due to either the desorption or reorientation of the CN species. The latter would better explain the UPS result, because the 6 eV peak was indeed enhanced to some extent at this temperature. The enhancement of the 6 eV peak could also be partially attributed to the formation of Si-C and Si-N bonds as observed in the UPS studies of other C or N containing species on Si substrates.<sup>19</sup> On the other hand, the 11.7 eV peak now shifted to 10.8 eV, should have some contribution from the NH bond.<sup>19</sup>

Further annealing the sample at 620 K caused a reduction of the 10.8 eV peak due to the partial cracking of the CH and NH bonds which was also observed in the HREEL spectra at the same temperature. At 800 K, both 6 eV and 10.8 eV peak intensities were attenuated and the 6 eV peak back shifted to 6.6 eV. By comparing with the corresponding HREELS results, these changes could be easily attributed to the further cracking of the CH and NH bonds and the breaking of the CN bond. Finally, at 1000 K, a hump at ~6 eV indicates some C and N species left on the surface.<sup>19</sup>

It is worth mentioning that Si-H species should give a peak at ~5.4 eV in UPS; however, in the present study this peak could be easily obscured by the adjacent, much stronger peak at 6 eV.

### 3. XPS

When 4 L HCN was dosed on a Si(100)-2x1 surface at 100 K, XP spectra presented peaks at 400.5 and 287.5 eV for N<sub>1s</sub> and C<sub>1s</sub> photoelectrons, respectively, as shown in Figures 7a and 7b. Compared with the corresponding HREELS results, these two peaks could be attributed to the dimeric and/or polymeric HCN on the surface. However, the noticeable tail at the lower binding energy side of both N<sub>1s</sub> and C<sub>1s</sub> peaks indicated the coexistence of a small amount of other species as discussed in the HREELS section. These observations are different from those of HCN adsorbed on Pt(111) at 220 K, in which two peaks with comparable intensities at 398.6 and 396.9 eV were produced for the N<sub>1s</sub> photoelectron,<sup>3</sup> corresponding to two different adsorption states.

As the 4 L HCN dosed Si(100) was warmed to 220 K, both C<sub>1s</sub> and N<sub>1s</sub> peak intensities decreased by ~70%, indicating the desorption of a significant amount of adsorbates. Meanwhile, both peaks also shifted towards lower binding energy and broadened substantially. The C<sub>1s</sub> peak could nearly be resolved into two peaks at 287.5 and 285.5 eV. The broadening of both C<sub>1s</sub> and N<sub>1s</sub> peaks obviously suggested

that more than one species adsorbed on the surface at 220 K. At this temperature, according to our HREELS measurements, two major species, i.e., CN and HCNH radicals, could be identified, explaining the observed broad C<sub>1s</sub> and N<sub>1s</sub> peaks.

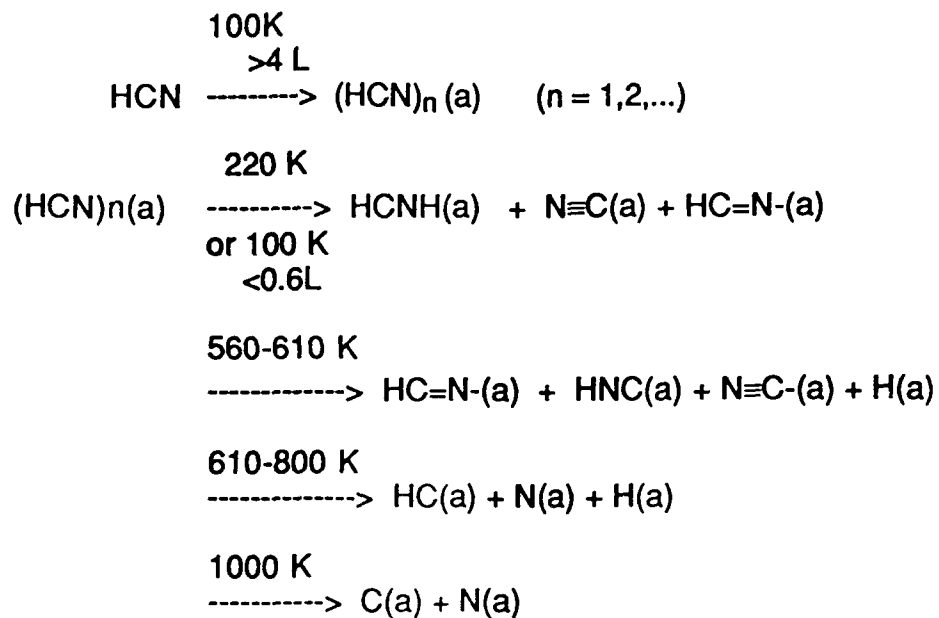
Annealing the sample to 550 K induced the following changes in the C<sub>1s</sub> and N<sub>1s</sub> XPS signals. The C<sub>1s</sub> spectrum became one broad peak centered at 285.3 eV with no obvious change in its intensity; while the N<sub>1s</sub> peak shifted to 398.3 eV and narrowed to some extent with the peak intensity further reduced by ~10%. Since there was little intensity change in the C<sub>1s</sub> peak, the attenuation of the N<sub>1s</sub> peak would result mainly from the reorientation of the CN radical from the end-on to the side-on adsorption geometry, rather than the desorption of the adsorbates. The narrowing of the N<sub>1s</sub> peak is also consistent with such an argument, because the chemical environment of the N atom in the side-on CN adspecies is more similar to that of the N atom in the side-on HCNH adspecies than the end-on CN radical. The C<sub>1s</sub> signal should be expected to increase as the CN group reoriented on the surface, because of the reduced suppression by the on-top N atom moving down onto the surface. This effect is probably weak, especially considering the rather weak C<sub>1s</sub> signal in the present study which is not clearly observed here. In addition, such an effect may be cancelled by a slight desorption of the adsorbates at this temperature. The reorientation of the CN radical was also indicated in the corresponding HREELS and UPS results, i.e., the attenuation of the 260 meV peak due to the end-on CN radical in HREELS and the enhancement of the 6 eV peak due partially to the further formation of Si-N bonds in UPS.

Annealing the sample at 680 K caused a partial breaking of the CN bond. The N<sub>1s</sub> peak was broadened and shifted closer to the value of 397.4 eV taken from a SiN sample.<sup>19,29</sup> Similarly, the C<sub>1s</sub> peak also became broader and shifted to a lower binding energy with an obvious contribution from the 283.3 eV component, which dominated the higher temperature spectra. Further annealing the sample to 800 K

narrowed the  $N_{1s}$  and  $C_{1s}$  XPS peaks and shifted them to 397.4 and 283.3 eV, respectively. Since these two values are close to those taken from silicon nitride<sup>29</sup> and silicon carbide<sup>30</sup> samples, respectively, the changes indicate the dissociation of the CN bond and the formation of Si-N and Si-C bonds, i.e. the formation of atomic C and N species on the surface, in consistence with the corresponding HREELS and UPS results.

## Summary

The interaction of HCN (DCN) with Si(100)-2x1 was studied in the temperature range 100-1000 K with HREELS, UPS and XPS. At 100 K with higher HCN dosages ( $D > 4L$ ), more than one adsorbed species exist on the surface with the HCN dimer and/or polymers being dominant, as indicated by the rather complicated HREELS and the broader peaks in both XPS and UP spectra. After warming the sample to 220 K, the HREEL spectrum resembles that obtained with a lower HCN dosage ( $< 0.6L$ ). At this temperature the major species on the surface could be identified as the CN and HCNH radicals with a possible small amount of  $HC=N$  adspecies, according to the HCN (DCN) HREELS results, which could also explain the corresponding UPS and XPS data. At 560 K, the 260 meV peak in HCN (DCN) HREELS was substantially attenuated, the 6 eV peak in UPS enhanced and the  $N_{1s}$  XPS peak intensity decreased, while that of the  $C_{1s}$  peak remained essentially unchanged. These observations are attributable most likely to the reorientation of the CN radical from the end-on to the side-on adsorption geometry. At 600-800 K, NH, CH and CN bond breaking occurred on the surface and the resulting CH, N and H species could be identified on the surface. Above 1000 K, only C and N species remained on the surface following the complete breaking of the CH bond and the desorption of the H species. The interaction between HCN and Si(100) can be summarized in the following scheme:



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Table II. Known Vibrational Frequencies of Some CN-Containing Species

Mode	HCN (DCN) <sup>a</sup>	HCNH <sup>b</sup>	C <sub>2</sub> N <sub>2</sub> <sup>c</sup>
$\nu_{\text{NH}}$	447(342)	407	
$\nu_{\text{CH}}$		364	
$\nu_{\text{CN}}$	252(241)	190	$\nu_{\text{a}}$ 289 $\nu_{\text{s}}$ 268
$\nu_{\text{CC}}$			105
$\delta_{\text{HNC}}$	65(50)		
$\delta_{\text{NH}}$		148	
$\delta_{\text{CH}}$		123	$\delta_{\text{a}}$ 62
$\delta_{\text{C=N}}$		115	$\delta_{\text{s}}$ 29

a. Ref. 25

b. Ref. 24

c. M.E. Jacox; J. Phys. Chem. Ref. Data; 6(1977) 1069.

## Figure Captions

- Figure 1: HREELS of HCN on Si(100)-2x1 at 100 K with the indicated dosages. The spectrum at the top-left corner was recorded with a higher resolution electron beam (FWHM = 6 meV in the straight through mode) to show the 28 meV mode derived from the intermolecular torsional vibration.
- Figure 2: HREELS of 4.5 L HCN on Si(100)-2x1 dosed at 100 K and then annealed at the indicated temperatures (Note: for visual clarity, figure has been broken into 2a and 2b).
- Figure 3: HREELS of 4.5 L DCN on Si(100)-2x1 dosed at 100 K and then annealed at the indicated temperatures (Note: figure has been broken into 3a and 3b for visual clarity).
- Figure 4: HREELS of 0.4 L HCN on Si(100)-2x1 dosed at 100 K and then annealed at the indicated temperatures. (Note: For visual clarity, figure has been broken into 4a and 4b.)
- Figure 5: HREELS of 0.4 L HCN dosed Si(100) at 100 K taken in the specular and 12° off specular modes, respectively.
- Figure 6: HE II UPS of 1.5 L HCN on Si(100)-2x1 dosed at 100 K and then annealed at the indicated temperatures. All curves are the differential spectra (see text).
- Figure 7: XPS of (a) N<sub>1s</sub> and (b) C<sub>1s</sub> photoelectrons taken from 4 L HCN on a Si(100)-2x1 sample; dosed at 100 K and then annealed at the indicated temperatures.

Fig. 2a

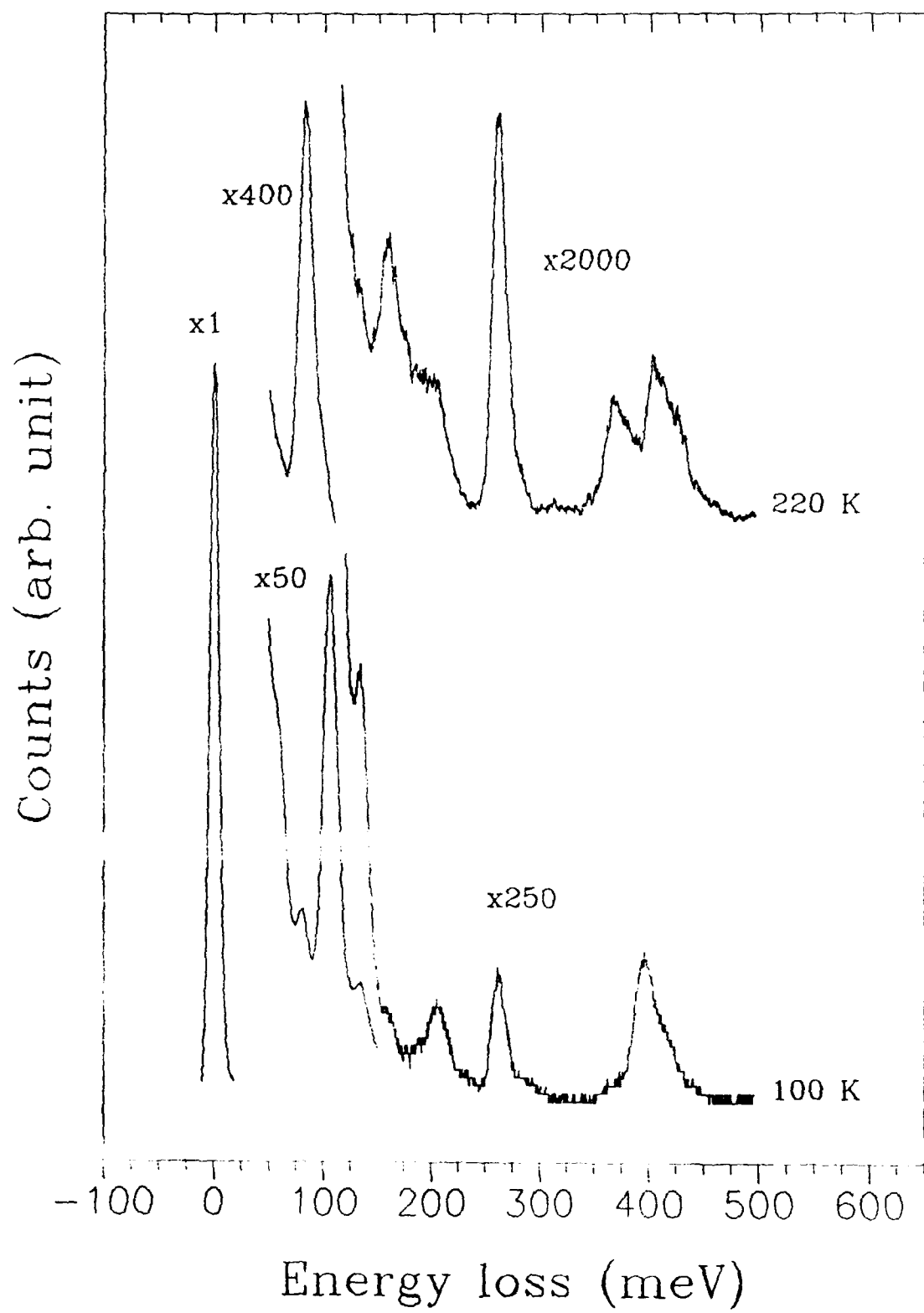


Fig. 2b

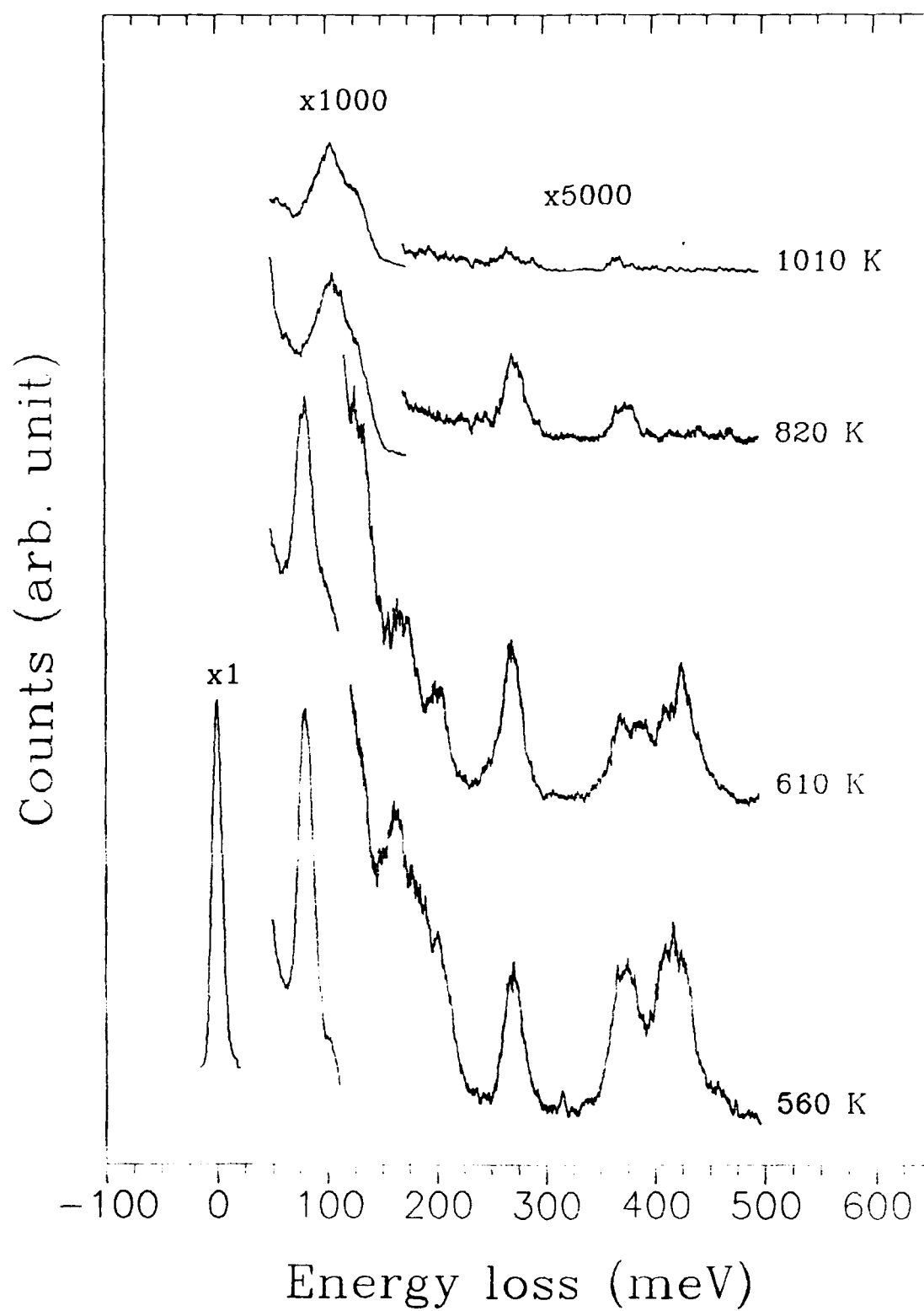


Fig. 3a

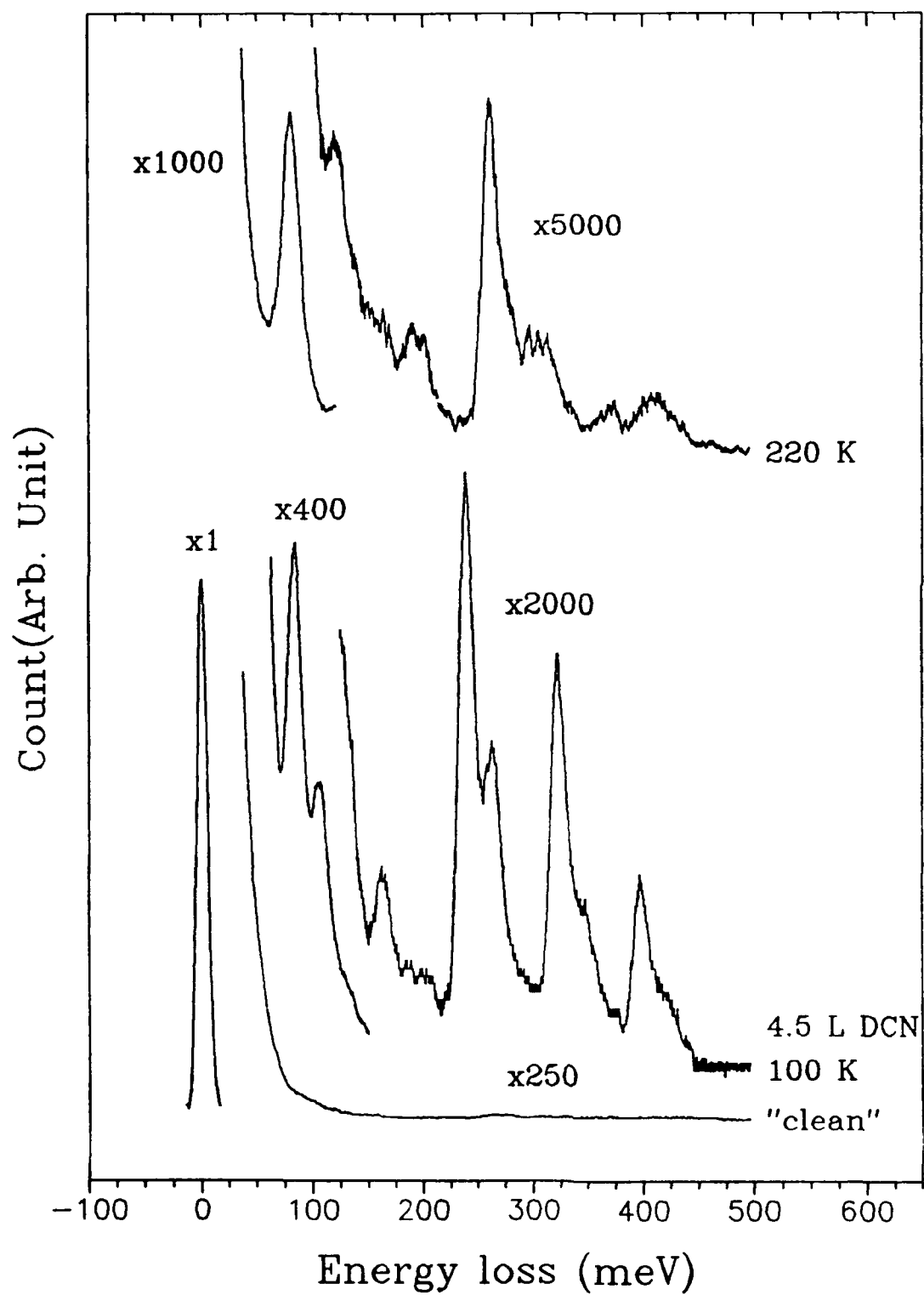


Fig. 3b

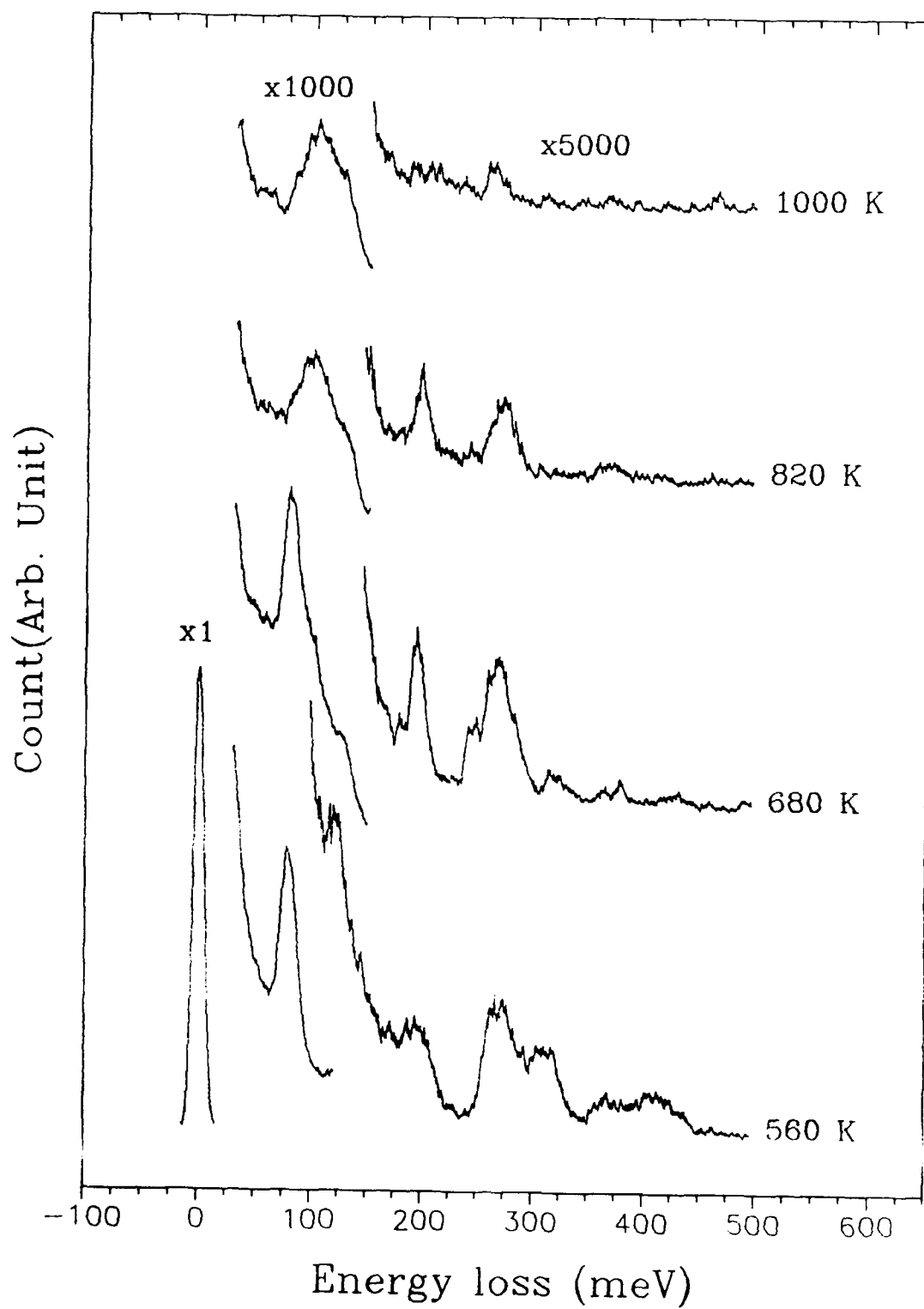
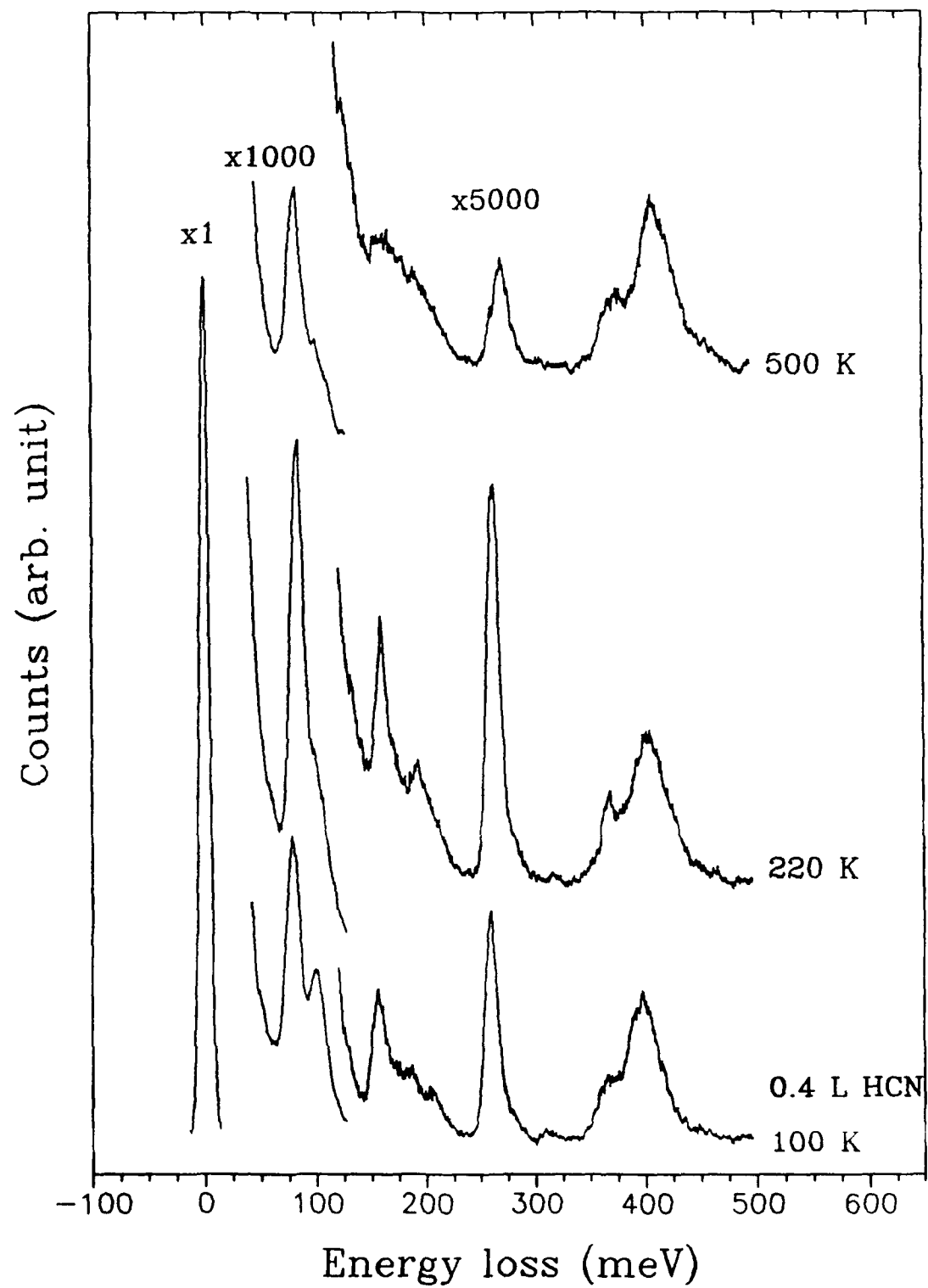




Fig. 4a



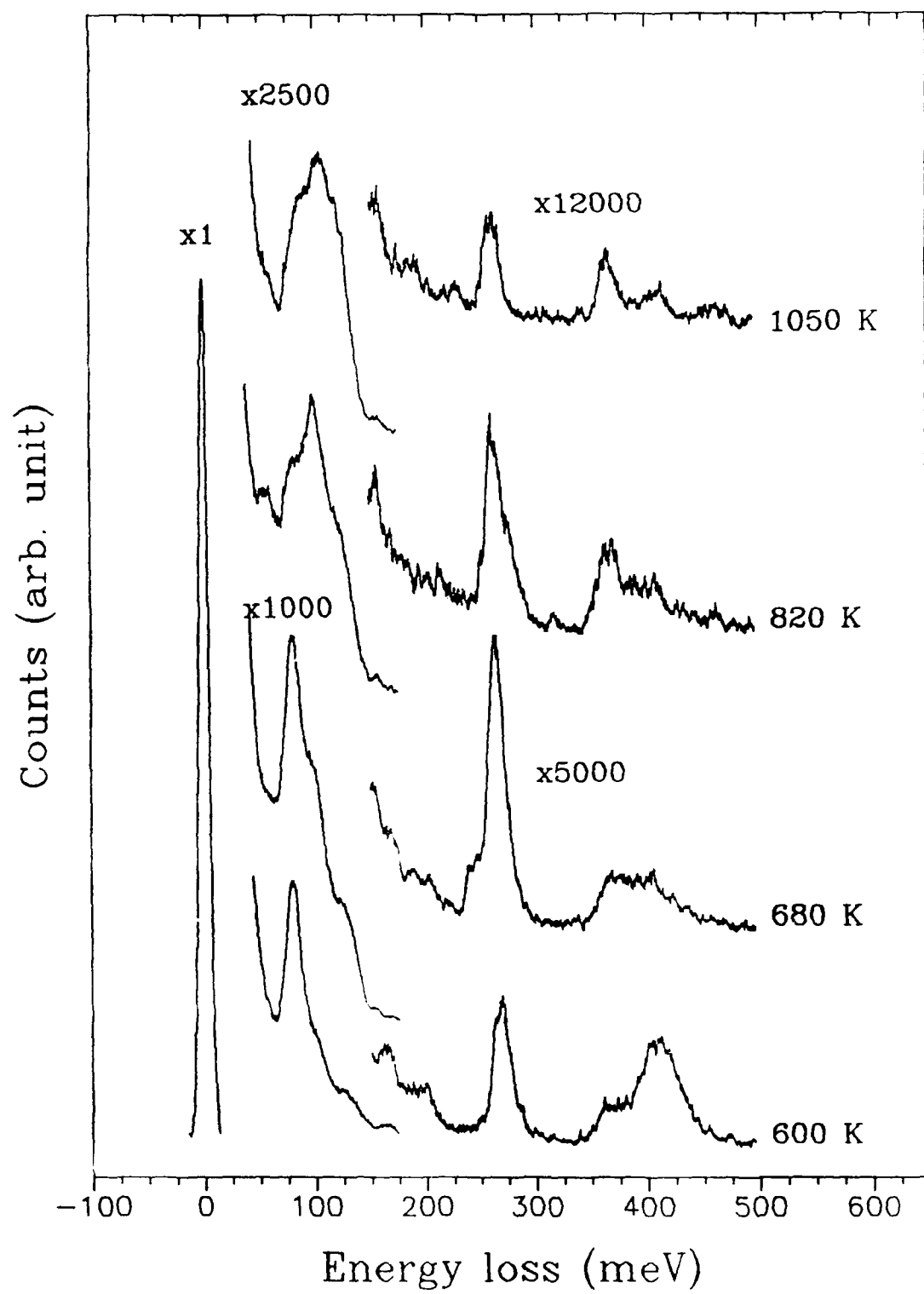


Fig. 5

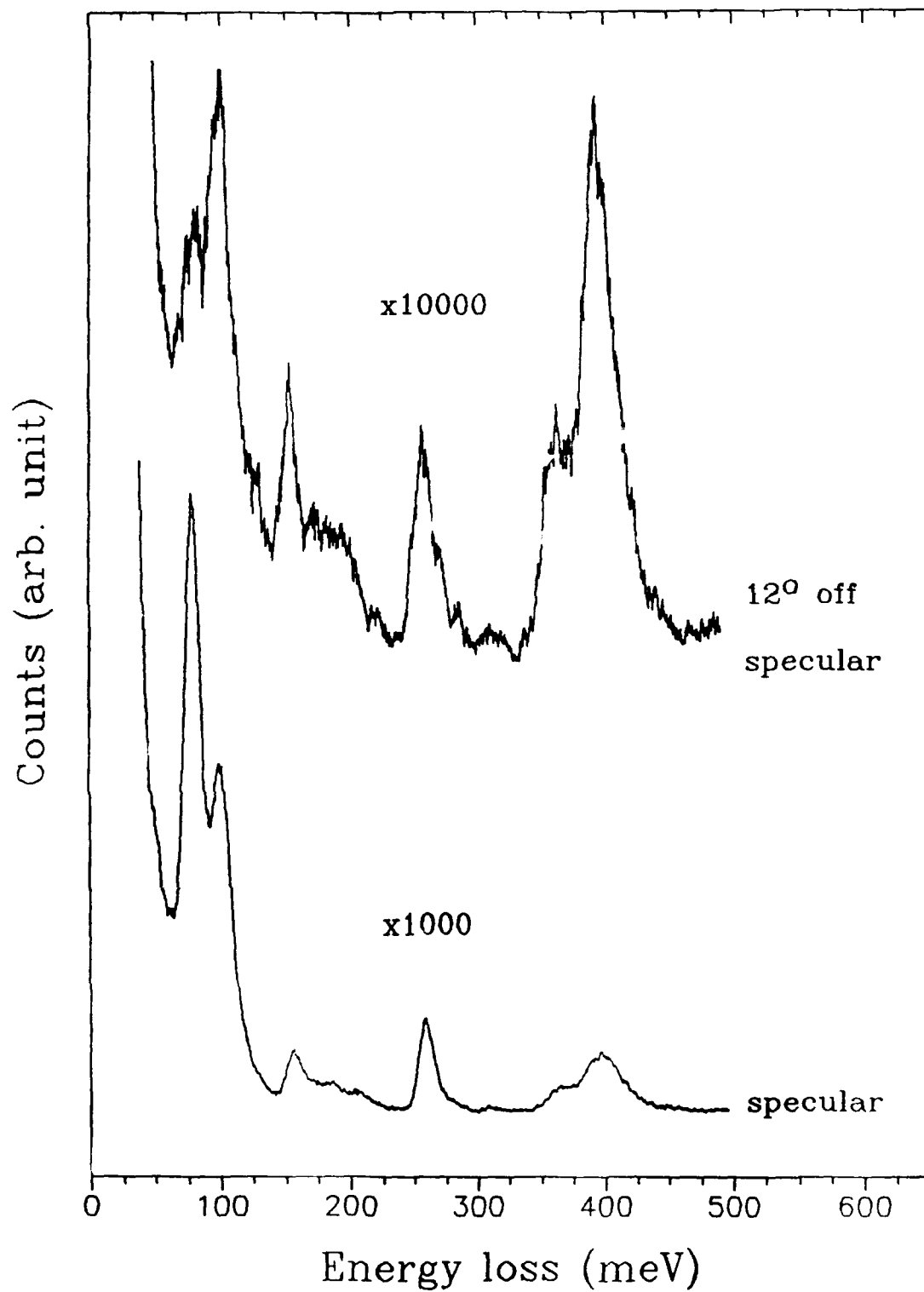


Fig. 6

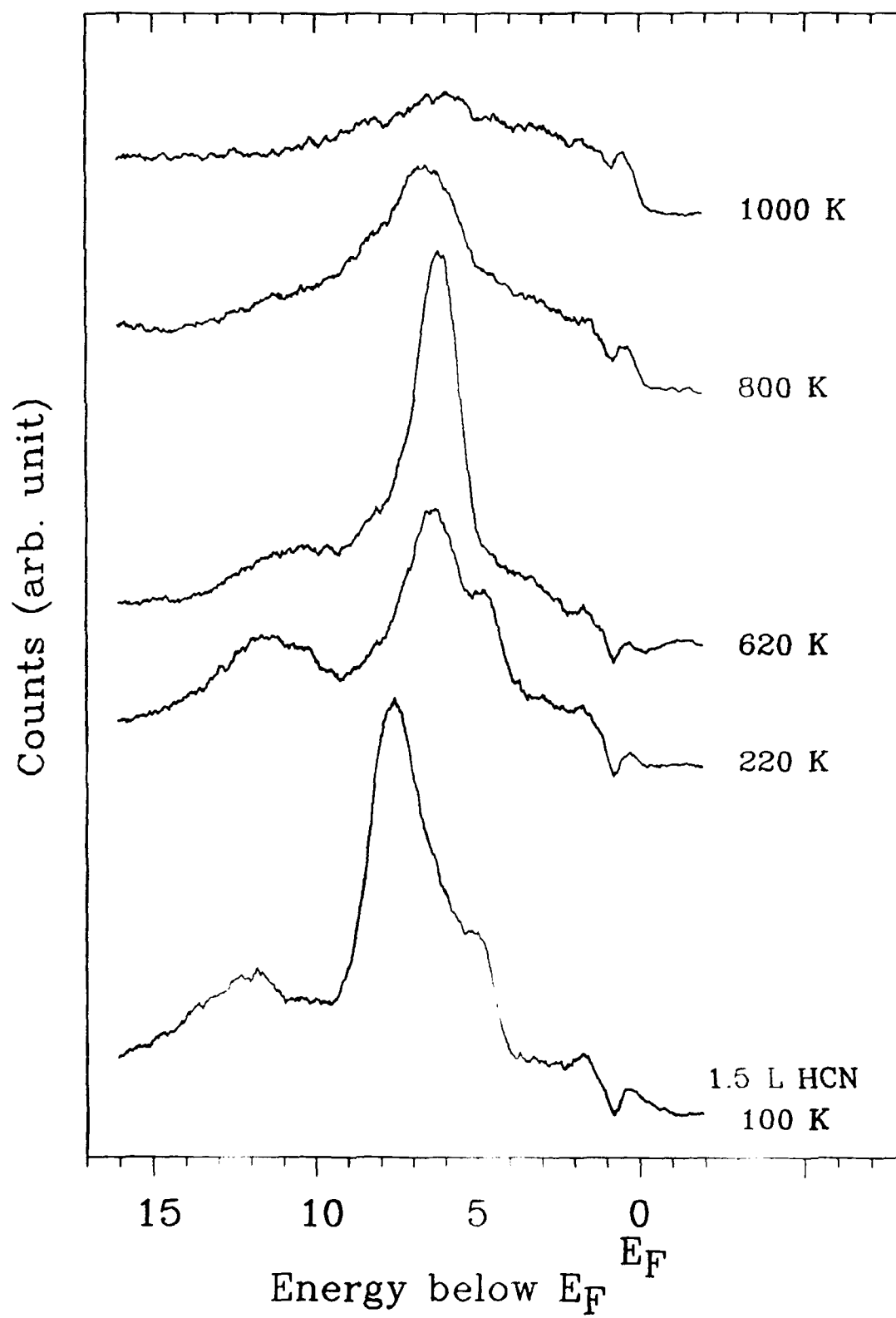


Fig. 7a

